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14. ABSTRACT
This is a comprehensive theoretical research program to investigate the fundamental principles of small-system thermodynamics (a.k.a. nanothermodynamics). The proposed work is motivated by our desire to better understand the fundamental dynamics and thermodynamics of hotspot formation and propagation in energetic materials. A better understanding of systems that are nanoscale and smaller that are either isolated or embedded in bulk can provide an improved understanding of initiation and reaction propagation criticality (that is, hotspots) in miniaturized and precisely engineered high energy density materials. The proposed work will improve our

15. SUBJECT TERMS
hotspots, small-system thermodynamics, nanoenergetics, molecular dynamics

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a. REPORT	b. ABSTRACT	c. THIS PAGE			Donald Thompson
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Report Title

Final Report: Theoretical Studies of Small-System Thermodynamics in Energetic Materials

ABSTRACT

This is a comprehensive theoretical research program to investigate the fundamental principles of small-system thermodynamics (a.k.a. nanothermodynamics). The proposed work is motivated by our desire to better understand the fundamental dynamics and thermodynamics of hotspot formation and propagation in energetic materials. A better understanding of systems that are nanoscale and smaller that are either isolated or embedded in bulk can provide an improved understanding of initiation and reaction propagation criticality (that is, hotspots) in miniaturized and precisely engineered high-energy-density materials. The proposed work will improve our fundamental knowledge of energy localization and energy transfer for various physical situations germane to traditional and nanoscale energetic formulations. It is based on atomic-scale simulation methods – primarily molecular dynamics with realistic force fields – and consists of fundamental studies of atomic and molecular clusters, nanoparticles, and single- and multi-component condensed phases for materials ranging in complexity from simple atomic systems through molecular explosives and interfaces between explosive constituent materials. Exploring how the fundamental thermodynamic properties and energy redistribution processes depend on system size, thermodynamic phase, or system dimensionality will contribute to understanding the detailed interactions that might be useful in the design of advanced energetic formulations. The energetic compounds of prime focus will be nitromethane, PETN, TATB, and cyclic nitramines; however, we may also study other systems, for example inorganic salts, as indicated by our results to further explore fundamental issues.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received		Paper
01/04/2016	4.00	Mehrdad Khanpour, Luis A. Rivera-Rivera, Thomas D. Sewell. On statistical mechanics of small systems: accurate analytical equation of state for confined fluids, Physics and Chemistry of Liquids, (02 2015): 467. doi: 10.1080/00319104.2015.1006631
09/19/2014	3.00	Luis A. Rivera-Rivera, Ali Siavosh-Haghighi, Thomas D. Sewell, Donald L. Thompson. A molecular dynamics study of the relaxation of an excited molecule in crystalline nitromethane, Chemical Physics Letters, (07 2014): 120. doi:
TOTAL:		**2**

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received		Paper
TOTAL:		

Number of Papers published in non peer-reviewed journals:

(c) Presentations

1. [Poster] Luis A. Rivera-Rivera, Ali Siavosh-Haghighi, Thomas D. Sewell, and Donald L. Thompson, “Single molecule relaxation in crystalline Nitromethane,” American Physical Society Prairie Section Fall 2013 Meeting, 7-9 November, 2013, Columbia, MO.

2. Invited talk, Thomas Sewell (Co-PI): "Atomic-Scale Theoretical Studies of Fundamental Properties and Processes in Molecular Materials under Static and Dynamic Compression" 2013 Fall ACS COMP Symposium: "Chemical Mechanisms in Advanced Materials" in the Materials Design and Multiscale Simulations session. Sept. 7-10, 2013

3. Thomas D. Sewell: Invited Colloquium Speaker, University of Illinois at Urbana-Champaign, 12 July 2014; “A molecular dynamics study of the relaxation of an excited molecule in crystalline nitromethane,” Luis A. Rivera-Rivera, Ali Siavosh-Haghighi, Thomas D. Sewell, Donald L. Thompson.

4. Shan Jiang: American Chemical Society Midwest Regional Meeting, Columbia, Missouri, 2014; “Molecular Dynamics Simulations of the Solid-Liquid Interface of Nitromethane,” Shan Jiang, Thomas D. Sewell and Donald L. Thompson.

5. Shan Jiang: 19th Biennial Conference of the APS Topical Group on Shock Compression of Condensed Matter (SCCM-2015) Tampa, Florida, 2015; “Molecular Dynamics Simulations of the Solid-Liquid Interface of Nitromethane,” Shan Jiang, Thomas D. Sewell and Donald L. Thompson.

Number of Presentations: 5.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

None.

Graduate Students

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Shan Jiang	0.54
FTE Equivalent:	**0.54**
Total Number:	**1**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Donald L. Thompson	0.30	
Thomas D. Sewell	0.06	
FTE Equivalent:	**0.36**	
Total Number:	**2**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

NAME
Total Number:

Names of personnel receiving PHDs

NAME
Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED
Win Grace	0.06
FTE Equivalent:	**0.06**
Total Number:	**1**

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See Attachment.

Technology Transfer

Scientific Progress and Accomplishments

This project focused on investigations of fundamental small-system thermodynamics (aka nano-thermodynamics) in organic energetic materials. The practical motivation was to better understand the fundamental dynamics and thermodynamics of hotspot formation and propagation of chemistry in energetic materials. Thus, we focused on the behavior of regions within a bulk material that initially is not in thermodynamic equilibrium with the surrounding material. We used classical molecular dynamics simulations to investigate fundamental properties at the atomic level. Two basic types of "nano-regions" were considered: Small numbers (including one) of molecules in a solid and interfaces between a solid and a liquid.

We completed three studies; two of which have been published and the third in a manuscript to be submitted for publication. The first study investigated the relaxation of an excited molecule in solid nitromethane. In the second study analytical expressions for the equations of state of simple systems were developed and compared to molecular dynamics results. In the third study we characterized equilibrium interfaces, studied the effects on heat flow (Kapitza resistance) through interfaces, and the effects of interfaces on shock fronts. Abstracts of the articles and the manuscript follow.

A molecular dynamics study of the relaxation of an excited molecule in crystalline nitromethane, Luis A. Rivera-Rivera, Ali Siavosh-Haghighi, Thomas D. Sewell, Donald L. Thompson; Chemical Physics Letters, Vol. 608, 21 July 2014, Pages 120-125; doi:10.1016/j.cplett.2014.05.065.

Abstract: Classical molecular dynamics simulations were used to study the relaxation of an excited nitromethane molecule in perfect crystalline nitromethane at 250 K and 1 atm pressure. The molecule was instantaneously excited by statistically distributing energy E^* between 25.0 kcal/mol and 125.0 kcal/mol among the 21 degrees of freedom of the molecule. The relaxation occurs exponentially with time constants between 11.58 ps and 13.57 ps. Energy transfer from the excited molecule to surrounding quasi-spherical shells of molecules occurs concurrently to both the nearest and next-nearest neighbor shells, but with more energy per molecule transferred more rapidly to the first shell.

On Statistical Mechanics of Small Systems: Accurate Analytical Equation of State for Confined Fluids, Mehrdad Khanpour, Luis A. Rivera-Rivera, Thomas D. Sewell; Physics and Chemistry of Liquids: An International Journal, Vol. 53 No. 4, 467-480, 2015. Doi: 10.1080/00319104.2015.1006631.

Abstract: Some relations are derived using statistical mechanics to describe the effects of surroundings on the properties of systems for sizes below the thermodynamic limit. A general expression for the free energy of closed, small systems is derived and then used to obtain the dependence of the thermal properties on density and temperature, including general expressions for equations of state and internal energies. Comparisons between predictions of the current theory and the results of molecular dynamics (MD) simulations are made for 3D hard-sphere and Lennard-Jones fluids for which the surroundings are

modelled as reflecting hard walls that confine the system along one direction. The analytical predictions are in excellent agreement with the MD results.

Molecular dynamics simulations of shock wave propagation across the crystal-melt interface of nitromethane, Shan Jiang, Thomas D. Sewell, and Donald L. Thompson; manuscript in preparation.

Abstract: Molecular dynamics (MD) simulations were used to study shock wave passage with normal incidence across the interface between (100)-oriented nitromethane in equilibrium with the melt. The simulations were performed using the fully flexible, non-reactive SRT force field [Sorescu, Rice, and Thompson, J. Phys. Chem. B **104**, 8406 (2000)]. A reverse-ballistic geometry was used wherein the sample containing the interface was impacted onto a rigid, stationary piston for the cases of shock propagation in both directions, that is, for shocks initiated in the crystal and transmitted into the liquid and *vice versa.* In all cases the piston was composed of the same phase as the material that impacted it, for example, liquid for the case of shock propagation from the liquid into the crystal. The local kinetic energies (intermolecular, intramolecular, and total) and stress states differ significantly between the liquid and crystal regions and also depend on whether the shock was initiated in the crystal or liquid. The overall number and spatial distribution of shock-induced molecular orientational defects in the crystal for shocks initiated in the crystal are similar to these obtained for analogous simulations for a pure crystal sample (no interface). By contrast, substantial differences in the extent and distribution of shock-induced orientational defect structures in the crystal region were observed when the shock was initiated in the liquid. Analysis of the mechanical states of the system for the two shock directions show that the damaged crystal resulting from initiation of the shock in the crystal is less able to support shear stresses than when the shock is initiated in the liquid.